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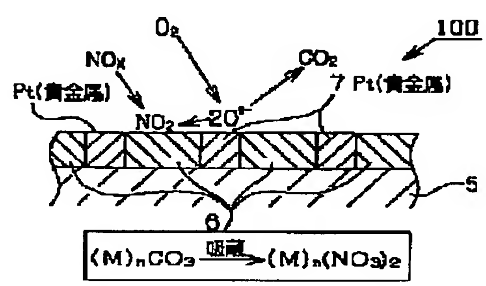
(54) EXHAUST EMISSION CONTROL METHOD IN INTERNAL COMBUSTION ENGINE

(57) Abstract:

PROBLEM TO BE SOLVED: To promote exhaust purification by comprehending the amount of nitrogen oxides occluded based on the change in oxygen concentration of the exhaust gas detected by oxygen sensors disposed upstream and downstream of nitrogen oxide occlusion reduction catalyst, so as to appropriately obtain the occlusion amount of nitrogen oxides in the catalyst and by selecting the air excess ratio.

SOLUTION: A nitrogen oxides occlusion reducing catalyst 100 carries a first component 6 of carbonate $(M)_nCO_3$ and a second component 7 of a noble metal such as platinum on a heat resistance base material 5. When an excess air ratio is in a lean state, oxygen ion and NOX react with each to form NO_2. Then the NO_2 reacts with carbonates, which is adsorbed to the catalyst 100 to form nitrates. When the nitrates reaches a saturation point, the NOX is desorbed and decomposed after reacting with unburned HC and CO. The change in the oxygen concentration is detected by oxygen sensors at the upstream and downstream sides. When an estimated ratio of NOX occlusion reaches a prescribed value, the air excess ratio is selected from lean to rich state. It is also estimated whether or not the nitrates have been completely desorbed from the catalyst 100, the air excess ratio is selected from rich to lean state.



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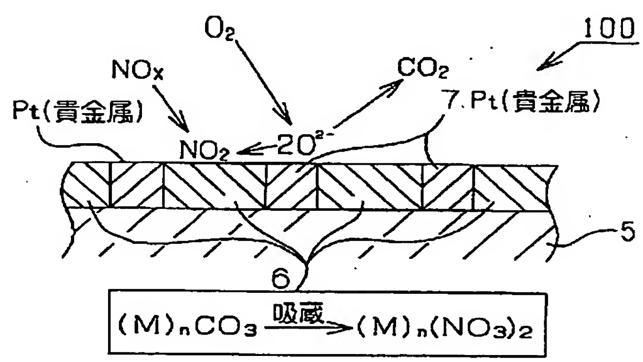
(54)【発明の名称】　内燃機関における排気ガスの浄化方法

(57)【要約】
【課題】　排気ガス中の窒素酸化物の浄化を促進する排気ガスの浄化方法を提供することである。
【解決手段】　第１成分に吸蔵された窒素酸化物を脱離するために空気過剰率をリーンからリッチへ切り替えた際に、窒素酸化物吸蔵還元触媒の上流側と下流側にそれぞれ設置した酸素センサにより排気ガス中の酸素濃度の変化を検出し、前記酸素濃度の変化で窒素酸化物の脱離量を推定し、前記脱離量が予め設定した値に達すると空気過剰率をリッチからリーンへ切り替える。



【特許請求の範囲】

【請求項１】　炭酸塩からなる第１成分と貴金属の単体または酸化物または複合酸化物からなる第２成分とを備えた窒素酸化物吸蔵還元触媒により化学量論比より酸素量が過剰な条件においては排気ガス中の窒素酸化物を二酸化窒素に変化させかつ前記第１成分に前記二酸化窒素を吸蔵させ、化学量論比より酸素量が不足する条件においては二酸化窒素を吸蔵させた前記第１成分から二酸化窒素を脱離させかつ排気ガス中の一酸化炭素、炭化水素で脱離させた前記二酸化窒素を還元する窒素酸化物吸蔵還元触媒において、

前記第１成分に吸蔵された窒素酸化物を脱離するために空気過剰率をリーンからリッチへ切り替えた際に、窒素酸化物吸蔵還元触媒の上流側と下流側にそれぞれ設置した酸素センサにより排気ガス中の酸素濃度の変化を検出し、前記酸素濃度の変化で窒素酸化物の脱離量を推定し、前記脱離量が予め設定した値に達すると空気過剰率をリッチからリーンへ切り替えることを特徴とする内燃機関における排気ガスの浄化方法。

【請求項２】　予め設定した基準温度と窒素酸化物吸蔵還元触媒の下流側の排気ガス温度との差に所定の係数を乗じて窒素酸化物吸蔵還元触媒の下流側酸素センサの出力電圧値に加算して前記下流側酸素センサの出力電圧値を補正し、前記下流側酸素センサ周辺の排気ガス温度に関わらず正確な酸素濃度を検出する請求項１に記載の内燃機関における排気ガスの浄化方法。

【請求項３】　窒素酸化物吸蔵還元触媒の窒素酸化物吸蔵容量に対する実際の窒素酸化物吸蔵量の比が所定値になるまでの時間を空気過剰率をリーンに設定して機関を稼動させる時間に設定し、かつ、窒素酸化物吸蔵還元触媒の窒素酸化物吸蔵容量に対する窒素酸化物の実際の脱離量の比が所定値になるまでの時間を空気過剰率をリッチに設定して機関を稼動させる時間に設定する請求項１に記載の内燃機関の排気ガスの浄化方法。

【請求項４】　窒素酸化物吸蔵還元触媒に吸蔵された窒素酸化物を脱離するために空気過剰率をリーンからリッチへ切り替える際に、前記切り替え後の空気過剰率を窒素酸化物の窒素酸化物吸蔵還元触媒からの脱離速度が速い領域のリッチな空気過剰率に設定する請求項１に記載の内燃機関における排気ガスの浄化方法。

【請求項５】　窒素酸化物吸蔵還元触媒に吸蔵された窒素酸化物を脱離させるために空気過剰率をリーンからリッチへ切り替える際に、トルク変動が小さいリッチな領域の空気過剰率で機関を稼動させる請求項１に記載の内燃機関における排気ガスの浄化方法。

【請求項６】　窒素酸化物吸蔵還元触媒に吸蔵された窒素酸化物を脱離させるために空気過剰率をリーンからリッチへ切り替えた際に、点火時期を遅角することにより窒素酸化物吸蔵還元触媒の温度を上昇させ窒素酸化物及び又は硫黄酸化物の脱離を促進する請求項１に記載の内燃機関の排気ガスの浄化方法。

【請求項７】　機関を停止させる前に空気過剰率 λ を排気ガス温度が高温となる λ ＝１．０付近で一定時間稼動させる請求項１に記載の内燃機関の排気ガスの浄化方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、内燃機関の排気ガスの浄化方法に関するものである。

【０００２】

【従来の技術】一般に、内燃機関の排気ガス中に含まれる窒素酸化物を浄化させるために窒素酸化物吸蔵還元触媒が利用されている。窒素酸化物吸蔵還元触媒に窒素酸化物を吸蔵させるために空気過剰率をリーンに設定し、また、吸蔵した窒素酸化物を脱離させかつ空気（排気ガス）中の一酸化炭素、炭化水素と反応させて浄化するために空気過剰率をリッチに設定する。

【０００３】ところが、窒素酸化物吸蔵還元触媒に吸蔵することができる窒素酸化物の量には限度があり、従来はこの吸蔵容量を把握せず、ただ一定時間が経過すると空気過剰率をリッチあるいはリーンに切り替えていた。

【０００４】そのため、窒素酸化物吸蔵還元触媒の吸蔵容量を超えて窒素酸化物を吸蔵しようとしても、排気ガス中の窒素酸化物は窒素酸化物吸蔵還元触媒を素通りしてしまい、大気中に放出されてしまう。また、窒素酸化物吸蔵還元触媒から窒素酸化物（硝酸塩）の脱離が完了しているにも関わらず、空気過剰率をリッチの設定のままで機関を稼動させると、熱効率の低下を招いてしまう。

【０００５】

【発明が解決しようとする課題】本発明は上記事情に鑑み、窒素酸化物吸蔵還元触媒の窒素酸化物の吸蔵容量を把握し、空気過剰率を適切にリーンからリッチに、またリッチからリーンに切り替えることにより、排気ガス中の窒素酸化物の浄化を促進する内燃機関における排気ガスの浄化方法を提供することを目的としている。

【０００６】

【課題を解決するための手段】請求項１の発明は、炭酸塩からなる第１成分と貴金属の単体または酸化物または複合酸化物からなる第２成分とを備えた窒素酸化物吸蔵還元触媒により化学量論比より酸素量が過剰な条件においては排気ガス中の窒素酸化物を二酸化窒素に変化させかつ前記第１成分に前記二酸化窒素を吸蔵させ、化学量論比より酸素量が不足する条件においては二酸化窒素を吸蔵させた前記第１成分から二酸化窒素を脱離させかつ排気ガス中の一酸化炭素、炭化水素で脱離させた前記二酸化窒素を還元する窒素酸化物吸蔵還元触媒において、前記第１成分に吸蔵された窒素酸化物を脱離するために空気過剰率をリーンからリッチへ切り替えた際に、窒素酸化物吸蔵還元触媒の上流側と下流側にそれぞれ設置し

た酸素センサにより排気ガス中の酸素濃度の変化を検出し、前記酸素濃度の変化で窒素酸化物の脱離量を推定し、前記脱離量が予め設定した値に達すると空気過剰率をリッチからリーンへ切り替えることを特徴とする内燃機関における排気ガスの浄化方法である。

【０００７】請求項２の発明は、予め設定した基準温度と窒素酸化物吸蔵還元触媒の下流側の排気ガス温度との差に所定の係数を乗じて窒素酸化物吸蔵還元触媒の下流側酸素センサの出力電圧値に加算して前記下流側酸素センサの出力電圧値を補正し、前記下流側酸素センサ周辺の排気ガス温度に関わらず正確な酸素濃度を検出する請求項１に記載の内燃機関における排気ガスの浄化方法である。

【０００８】請求項３の発明は、窒素酸化物吸蔵還元触媒の窒素酸化物吸蔵容量に対する実際の窒素酸化物吸蔵量の比が所定値になるまでの時間を空気過剰率をリーンに設定して機関を稼動させる時間に設定し、かつ、窒素酸化物吸蔵還元触媒の窒素酸化物吸蔵容量に対する窒素酸化物の実際の脱離量の比が所定値になるまでの時間を空気過剰率をリッチに設定して機関を稼動させる時間に設定する請求項１に記載の内燃機関の排気ガスの浄化方法である。

【０００９】請求項４の発明は、窒素酸化物吸蔵還元触媒に吸蔵された窒素酸化物を脱離するために空気過剰率をリーンからリッチへ切り替える際に、前記切り替え後の空気過剰率を窒素酸化物の窒素酸化物吸蔵還元触媒からの脱離速度が速い領域のリッチな空気過剰率に設定する請求項１に記載の内燃機関における排気ガスの浄化方法である。

【００１０】請求項５の発明は、窒素酸化物吸蔵還元触媒に吸蔵された窒素酸化物を脱離させるために空気過剰率をリーンからリッチへ切り替える際に、トルク変動が小さいリッチな領域の空気過剰率で機関を稼動させる請求項１に記載の内燃機関における排気ガスの浄化方法である。

【００１１】請求項６の発明は、窒素酸化物吸蔵還元触媒に吸蔵された窒素酸化物を脱離させるために空気過剰率をリーンからリッチへ切り替えた際に、点火時期を遅角することにより窒素酸化物吸蔵還元触媒の温度を上昇させ窒素酸化物及び又は硫黄酸化物の脱離を促進する請求項１に記載の内燃機関の排気ガスの浄化方法である。

【００１２】請求項７の発明は、機関を停止させる前に空気過剰率λを排気ガス温度が高温となるλ＝１．０付近で一定時間稼動させる請求項１に記載の内燃機関の排＊＊気ガスの浄化方法である。

【００１３】

【発明の実施の形態】図１は、請求項１～７の発明を実施するのに適した窒素酸化物吸蔵還元触媒１００（以下、触媒１００と呼ぶ）の概念図である。触媒１００は、コーディエライト等からなる耐熱性基材５にγアルミナからなる多孔質担体層を形成し、その多孔質担体層には、第１成分６として後述する化学式（$(M)_nCO_3$）で示される炭酸塩と第２成分７として白金Ｐｔ等の貴金属が担持されている。

【００１４】第１成分６である炭酸塩の化学式（$(M)_nCO_3$）において、記号Ｍで示した部分には、例えば、マンガン・鉄・コバルト・ニッケル・銅・銀・亜鉛・クロム・モリブデン・タングステン・バナジウム・ニオブ・タンタル・セリウム・ランタン・チタン・ジルコニウム等の遷移金属、カルシウム・マグネシウム・ストロンチウム・バリウム等のアルカリ土類金属、リチウム・ナトリウム・カリウム・ルビジウム・セシウム等のアルカリ金属、ランタン・イットリウム等の希土類、その他アルミニウム、けい素、スズ、鉛、リン、イオウのうちのいずれかが適用される。また、第２成分７としては白金Ｐｔ以外に、パラジウム、ロジウム、ルテニウム等の貴金属の単体、または酸化物、または複合酸化物よりなる成分を適用することができる。

【００１５】図１は、空気過剰率をリーン（希薄状態）に設定し、触媒１００に窒素酸化物（以下、NO_xと呼ぶ）を硝酸塩（NO_3塩）の形で吸蔵する過程を示している。図２は、空気過剰率をリッチ（過濃状態）に設定し、触媒１００に吸蔵された硝酸塩を触媒１００から脱離させ、浄化する過程を示している。

【００１６】図４は、第１成分６及び第２成分７を包含する触媒１００を排気管２の途中に設置した状態を示す正面図である。図４に示すように、機関１には排気管２が接続されており、排気管２の触媒１００を挟んで機関１に近い側には上流側酸素センサ３が設置されており、また、機関１から遠い側には下流側酸素センサ４が設置されている。

【００１７】空気過剰率λがλ_L（図３）に設定されたリーン状態（希薄状態）においては、触媒１００上では、図１に示すように酸素イオンO_2^-又はO^{2-}とNO_xが反応して二酸化窒素NO_2が生じ、NO_2は触媒１００の第１成分６である炭酸塩と反応し触媒１００の表面に吸着して硝酸塩を形成する。この時の反応式は、（１）式のように表される。

$$(M)_nCO_3+2NO_2+1/2O_2 \rightarrow (M)_n(NO_3)_2+CO_2 \cdots (1)$$

【００１８】触媒１００上の硝酸塩が飽和状態になると、図３に示すように、空気過剰率を$\lambda=\lambda_R$に設定　※※し、硝酸塩から窒素酸化物NO_xを脱離する。この時の反応式は、（２）式のように表される。

$$(M)_nCO_3+2NO_2+1/2O_2 \leftarrow (M)_n(NO_3)_2+CO_2 \cdots (2)$$

こうして脱離された窒素酸化物NO_xを排気ガス中に含まれている未燃の炭化水素ＨＣ、一酸化炭素ＣＯと反応させることにより、触媒１００上の硝酸塩を窒素N_2、二酸化炭素CO_2及び水H_2Oに分解して還元し、除去す

る。

【0019】式（2）は、式（1）において反応の進む方向が逆になったものである。ここで、空気過剰率をλ_L及びλ_Rに設定して機関1を稼動させる時間t_L及びt_Rを算出する方法を説明する。

【0020】図6に示すように、触媒100から硝酸塩の脱離を開始する際に、触媒100のNO_x吸蔵容量に対する実際の吸蔵量の割合（以下、NO_x吸蔵割合と呼ぶ。）が大きければ大きいほど脱離速度は速くなり、逆に吸蔵の割合が小さいと脱離速度は遅くなる。

【0021】式（2）に示すように、触媒100から硝酸塩が脱離する際には酸素も脱離する。その酸素の脱離量は、硝酸塩の脱離量に比例する。触媒100からの酸素の脱離速度が大きい場合は、触媒100の下流側の酸素濃度の減少する速度が遅くなる。この酸素濃度の変化を上流側酸素センサ3と下流側酸素センサ4により検出する。

【0022】上流側酸素センサ3及び下流側酸素センサ4により、それぞれ所定の出力電圧値V_dを検出した時期を記録し、上流側酸素センサ3がV_dを検出してから下流側酸素センサ4がV_dを検出するまでの時間を遅れ時間t_dと呼ぶ。この遅れ時間t_dは、NO_x吸蔵割合と比例関係にあり、NO_x吸蔵割合が大きくなるほど遅れ時間t_dも長くなる。

【0023】ところで、触媒100にNO_xを吸蔵させる際に、既に吸蔵されているNO_x量により吸蔵速度は変化する。すなわち、吸蔵量が多ければ吸蔵速度は遅く、吸蔵量が少なければ吸蔵速度は速い。したがって、ある程度吸蔵が進むと、まだ吸蔵する余地は残っていても吸蔵速度が遅くなり、効率よく吸蔵することができなくなる。そこで、NO_x吸蔵割合がある所定の割合になった際に、空気過剰率をリーンからリッチへ切り替える。その所定のNO_x吸蔵割合に対応する空気過剰率の切替時期（リーン設定時間）を次の式（3）により算出する。遅れ時間が一定値t_{dt}になるように制御すると、NO_x吸蔵割合が一定に保たれ、空気過剰率をリーン（λ_L）に設定する時間（t_L）を決定することができる。

$$t_{L(n+1)} = t_{L(n)} + C_1 \times \Sigma\ (t_{dt} - t_{d(i)}) / k_1 \cdots (3)$$

ここでiは、（$n-k_1+1$）〜nの自然数である。

【0024】遅れ時間を計測する際に、（n＋1）回目の遅れ時間$t_{L(n+1)}$は、n回目の遅れ時間$t_{L(n)}$に目標遅れ時間t_{dt}とi回目の遅れ時間との差をとって平均した値を加算して補正する。ここで、C_1は単位を揃える所定の係数であり、実験によりt_Lが一定の値に収束するように決定される。k_1は平均する（遅れ時間を計測した）回数、すなわち、空気過剰率をリーンからリッチに切り替えた切替回数である。

【0025】一方、空気過剰率をリッチ（λ_R）に設定した脱離過程では、硝酸塩が脱離している間は、式（2）に示すように酸素O_2も脱離している。硝酸塩の脱離速度は、触媒100に吸蔵されている硝酸塩の量に比例的であり、吸蔵量が多ければ脱離速度は速く、吸蔵量が少なければ脱離速度は遅くなる。したがって、酸素の脱離量の変化も硝酸塩の脱離量に追従するので、下流側酸素センサ4の出力電圧値により酸素濃度の変化を監視し、出力電圧値がV_{RRC}になると触媒100からの硝酸塩の脱離がほぼ完了したものと推定し、空気過剰率をリッチ（λ_R）からリーン（λ_L）に切り替える。

【0026】目標出力電圧値V_{RRCT}を予め実験を行って求めておく。この目標出力電圧値V_{RRCT}は、O_2及びNO_xの脱離が完了したことを示す指標となる。図8に示すように、下流側酸素センサ4の各回の出力電圧の最大値を$V_{RRC(i)}$とし、式（4）により次に空気過剰率をリッチ（λ_R）からリーン（λ_L）に切り替えるまでの脱離時間（空気過剰率をλ_Rに設定する時間）$t_{R(n+1)}$を算出する。

$$t_{R(n+1)} = t_{R(n)} + C_2 \times \Sigma\ (V_{RRCT} - V_{RRC(i)}) / k_2 \cdots (4)$$

ここでiは（$n-k_2$）〜nまでの自然数であり、C_2は単位を揃えるための係数であり、実験によりt_Rが一定の値に収束するように決定される。k_2は空気過剰率をλ_Rからλ_Lに切り替える切替回数であり、過去に行った切替のうちサンプリングした切替回数である。

【0027】下流側酸素センサ4は、触媒100を通過してきた排気ガスの温度の影響を受けて感度が変化してしまう。すなわち、排気ガスが高温であれば出力電圧は低くなり、逆に低温になれば出力電圧は高くなる。しかし、以下のように出力電圧値を補正することにより、排気ガス温度によらず適正な出力を得ることができる。

【0028】予め所定温度（例えば560℃）における下流側酸素センサ4の出力電圧の最大値を計測し、この値をV_{d0}とする。機関1を稼動させて実際に計測した下流側出力電圧の最大値V_dを式（5）により補正する。T_Rは下流側酸素センサ4付近の排気ガス温度である。

$$V_d = V_{d0} + C_3 \times (560 - T_R) \cdots (5)$$

ここでC_3は、実験でいくつかの温度に設定して計測した際の出力電圧を参考にして決定した所定の係数である。

【0029】目標出力電圧値V_{RRCT}も式（6）により補正し、排気ガス温度によって変化させる。

$$V_{RRCT} = V_{RRCT0} + C_4 \times (560 - T_R) \cdots (6)$$

ここでV_{RRCT0}は、排気ガス温度が560℃の際の目標出力電圧値である。

【0030】機関1が低負荷低回転で稼動中は排気ガス温度が低く、下流側酸素センサ4の出力電圧値は変動し易くなる。この場合は、式（7）及び（8）により空気過剰率の切替回数k_1、k_2をそれぞれk_{10}、k_{20}に補正する。

$k_{10}=k_1\times C_5$（５６０－T_R）・・・（７）

$k_{20}=k_2\times C_6$（５６０－T_R）・・・（８）

ここでC_5及びC_6は所定の係数である。

【００３１】触媒１００に吸蔵した硝酸塩を脱離するために空気過剰率をリーン（λ_L）からリッチ（λ_R）に切り替える際、脱離速度が速ければその分リッチで稼動させなければならない時間が短くなり、リーンで稼動させることができる時間が長くなる。図９に示すように、触媒１００からのＮＯｘの脱離速度は空気過剰率がリッチになるほど大きくなる。したがって、空気過剰率をリッチ（λ_R）に設定する際には、例えばλ_R＝０．８に設定する。λ_Rは、０．６５～０．９までの範囲内で設定すればよいが、０．７～０．８５の範囲内で設定するのがより好ましい。

【００３２】また、図１０に示すように、空気過剰率がλ＝１付近でトルク変動は最大となる。したがって、触媒１００から硝酸塩を脱離させる際には、トルク変動の大きいλ＝１付近を避けて、λ_Rを例えば０．８に設定する。トルク変動を小さくするために、λ_Rは０．６５～０．９までの範囲内で設定すればよいが、０．７～０．８５の範囲内で設定するのがより好ましい。

【００３３】図１１に示すように、点火時期を遅角するほど触媒１００の上流側の排気ガスの温度は高くなる。排気ガス温度が高いほど触媒１００からの硝酸塩の脱離速度は速くなるので、空気過剰率をリッチ（λ_R）に設定した際には点火時期を遅角させる。

【００３４】図１２に示すように、触媒１００の上流側のＮＯｘ流量は、負荷及び機関回転数が大きいほど大きくなる。また、負荷及び機関回転数が大きいほど触媒１００の上流側の排気ガス温度は高くなる。図１３に示すように、触媒１００のＮＯｘ吸蔵量はこの排気ガスの温度により変化する。

【００３５】（ＮＯｘ吸蔵量／ＮＯｘ吸蔵容量）がある値になるまでの時間（ＮＯｘがある程度吸蔵されるのに要する時間）は負荷及び機関回転数によらず（ＮＯｘ吸蔵容量／ＮＯｘ流量）に比例する。したがって、（ＮＯｘ流量／ＮＯｘ吸蔵容量）に比例するリーンカウンタ係数C_{Lt}に空気過剰率をリーン（λ_L）に設定する時間t_L（図３）を乗算した値を積算すると、その積算値は負荷、機関回転数によらず（ＮＯｘ吸蔵量／ＮＯｘ吸蔵容量）に比例する。

【００３６】よって、所定の（ＮＯｘ吸蔵量／ＮＯｘ吸蔵容量）の値に対応する（$C_{Lt}\times t_L$）の積算値を予め実験で求めておき、（$C_{Lt}\times t_L$）の積算値がその値になった際に空気過剰率をリーン（λ_L）からリッチ（λ_R）に切り替えると触媒１００はＮＯｘの吸蔵限界又は吸蔵限界に近い状態で脱離を開始することができ、排気ガス中のＮＯｘ浄化が非常に効率的になる。ここでt_Lは空気過剰率をリーン（λ_L）に設定しておく時間である。

【００３７】また、空気過剰率をリッチ（λ_R）に設定

した際に、触媒１００からのＮＯｘ脱離速度は、排気ガス温度が高くなると図１４に示すように速くなる。したがって、（ＮＯｘ脱離速度／ＮＯｘ吸蔵容量）に比例するリッチカウンタ係数C_{Rt}に空気過剰率をリッチ（λ_R）に設定する時間t_R（図３）を乗算して積算した値は、負荷及び機関回転数によらず（ＮＯｘ脱離量／ＮＯｘ吸蔵容量）に比例する。

【００３８】よって、所定の（ＮＯｘ脱離量／ＮＯｘ吸蔵容量）の値に対応する（$C_{Rt}\times t_R$）の積算値を予め実験で求めておき、（$C_{Rt}\times t_R$）の積算値がその値になった際に空気過剰率をリッチ（λ_R）からリーン（λ_L）に切り替える。これにより、触媒１００からほぼＮＯｘの脱離が完了し、吸蔵工程に移ることができる。

【００３９】図５に示すように、空気過剰率がリーン状態においては、ＮＯｘばかりでなく硫黄Ｓと酸素イオンO_2^-又はO^{2-}が反応して、触媒１００上に硫酸塩を形成して吸着（被毒）する。触媒１００上に硫酸塩が形成されると、その分だけ硝酸塩を吸蔵することができる領域が減少するため、ＮＯｘの吸蔵容量が小さくなってしまう。

【００４０】触媒１００からの硫酸塩の脱離速度は、触媒上流側の排気ガス温度が高いほど速くなる。したがって、排気ガス温度を高くするために点火時期を遅角すれば硫酸塩の脱離速度は速くなり、触媒１００のＮＯｘ吸蔵容量は元の容量に戻る。

【００４１】触媒１００に硝酸塩や硫酸塩が形成されている状態で稼動中の機関１（図４）を停止させると、触媒１００と硝酸塩及び硫酸塩が堅固に結合してしまうため、再度機関１を稼動させて触媒１００の温度が上昇してもこれらを脱離させることはできなくなる。したがって、稼動中の機関１を停止させる際には、ある一定時間（例えば１～５分間、好ましくは２～３分間）空気過剰率λを１．１～０．９、好ましくは１．０～０．９５の範囲に設定して稼動させ、吸蔵したＮＯｘや被毒した硫黄酸化物を脱離させてから停止させるようにする。

【００４２】以上の説明では、第２成分７であるＰｔ等の貴金属が直接耐熱性基材５に担持されている構成を踏まえて説明したが、図７に示すように、第２成分７は第１成分６に担持させてもよい。

【００４３】

【発明の効果】請求項１の発明を適用すると、排気ガス中の窒素酸化物の脱離量に比例する酸素の脱離量を酸素センサで検出するので、触媒１００への窒素酸化物の吸蔵量を推定することができ、触媒１００の吸蔵限界まで空気過剰率をリーンに設定して機関を稼動させた後リッチに切り替え、触媒１００からの窒素酸化物の脱離が完了した時点で空気過剰率をリッチからリーンに切り替えることができるので、触媒１００の窒素酸化物浄化性能を充分に発揮することができ、排気ガスを効率よく浄化することができる。また、空気過剰率をリッチに切り替

えて機関を稼動させる時間を必要最小限にすることができるので、熱効率を向上させることができる。

【００４４】請求項２の発明を適用すると、排気ガス温度が変動しても下流側酸素センサ４の検出結果を基準温度で計測した際の検出値に補正することができ、したがって排気ガス中の窒素酸化物の量を正確に推定することができる。

【００４５】請求項３の発明を適用すると、機関にかかる負荷や機関回転数が変化し窒素酸化物の流量が変化しても、触媒１００の窒素酸化物吸蔵容量に見合った吸蔵量を確保しかつ吸蔵した窒素酸化物を脱離させるように空気過剰率をリーンからリッチに適切に切り替えることができるので、排気ガス中の窒素酸化物を効率よく浄化することができる。

【００４６】請求項４の発明を適用すると、触媒１００からの窒素酸化物の脱離を迅速に行うことができ、空気過剰率をリッチに設定しておく時間を短くすることができるので、単位時間当たりの窒素酸化物の吸蔵量を増加させることができ、排気ガスの浄化を促進することができる、また、空気過剰率をリッチに設定しておく時間を短くすることにより、熱効率を向上させることができる。

【００４７】請求項５の発明を適用すると、トルク変動が小さいリッチな空気過剰率で機関１を稼動させるので、窒素酸化物の脱離を行う際にトルク変動を抑えることができる。

【００４８】請求項６の発明を適用すると、点火時期を遅角させ触媒１００の温度（排気ガスの温度）を上昇させるので、触媒１００から窒素酸化物の脱離を促進することができ、空気過剰率をリッチに設定しておく時間を短くすることができ、空気過剰率をリーンに設定して機関１を稼動させる時間を長くすることができるので、排気ガス中の窒素酸化物の浄化を促進することができ、また、熱効率を向上させることができる。

【００４９】請求項７の発明を適用すると、触媒１００に吸蔵されている窒素酸化物及び被毒した硫黄酸化物を脱離させた後に機関を停止するので、触媒１００がクリーンな状態に保たれ、窒素酸化物に対する吸蔵容量を充分に確保することができ、次回に機関１を稼動させた際に排気ガス中の窒素酸化物を効率よく浄化することができる。

【図面の簡単な説明】

【図１】　ＮＯxが触媒に吸蔵される過程を示す概念図である。

【図２】　触媒に吸蔵されたＮＯxが脱離される過程を示す概念図である。

【図３】　空気過剰率をリーン（λ_L）とリッチ（λ_R）との間で切り替える様子を示すグラフである。

【図４】　排気管に触媒と二つの酸素センサを設置した状態を示す側面略図である。

【図５】　硫黄酸化物が触媒を被毒する過程を示す概念図である。

【図６】　触媒へのＮＯxの吸蔵割合の大小による酸素脱離速度の違いを示すグラフである。

【図７】　（ａ）は図１において第２成分が第１成分に担持される状態を示す概念図である。（ｂ）は図２において第２成分が第１成分に担持される状態を示す概念図である。

【図８】　空気過剰率に対応する触媒下流側酸素センサの出力電圧値を示すグラフである。

【図９】　空気過剰率とＮＯxの触媒からの脱離速度の関係を示すグラフである。

【図１０】　空気過剰率と機関に発生するトルクの変動の大きさの関係を示すグラフである。

【図１１】　点火時期と触媒の上流側の排気ガス温度の関係を示すグラフである。

【図１２】　機関回転数と機関にかかる負荷と触媒上流側のＮＯx流量の関係を示すグラフである。

【図１３】　触媒上流の排気ガス温度とＮＯx吸蔵量の関係を示すグラフである。

【図１４】　触媒上流の排気ガス温度とＮＯxの触媒からの脱離速度の関係を示すグラフである。

【符号の説明】

３　　上流側酸素センサ

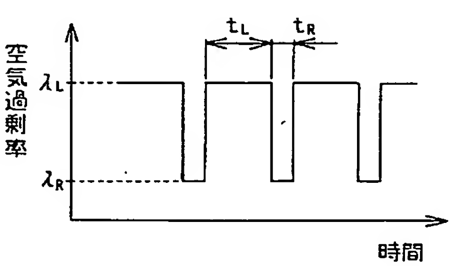
４　　下流側酸素センサ

６　　第１成分

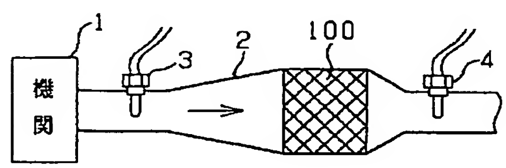
７　　第２成分

１００　触媒（窒素酸化物吸蔵還元触媒）

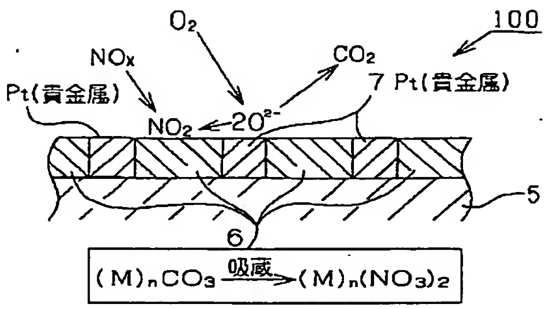
【図３】



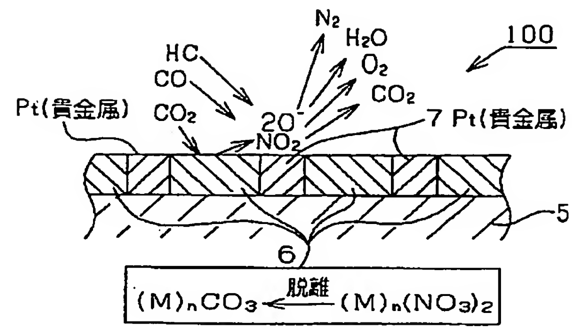
【図４】



【図１】



【図２】



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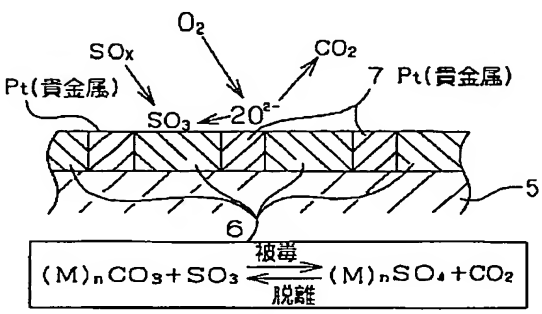

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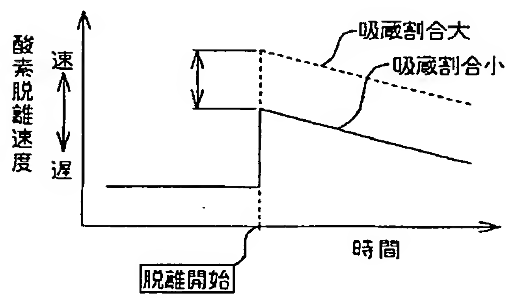

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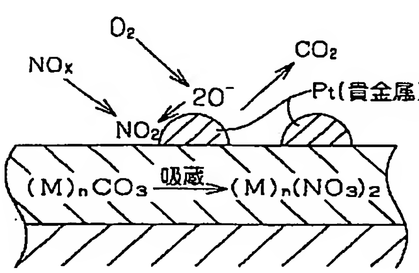

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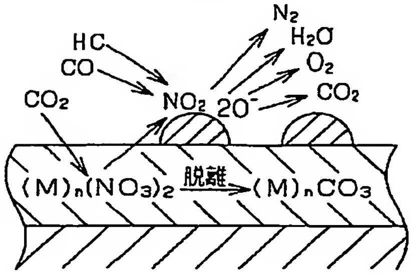

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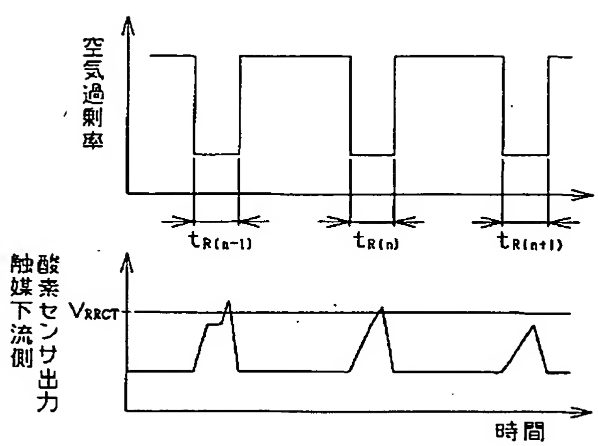

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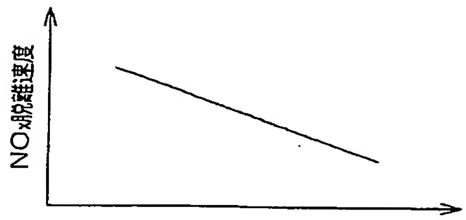

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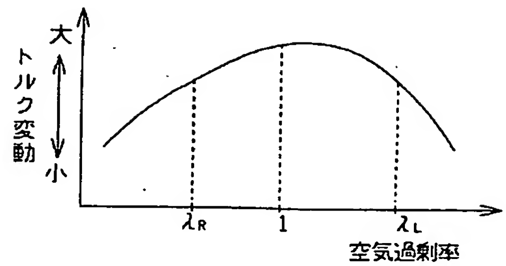

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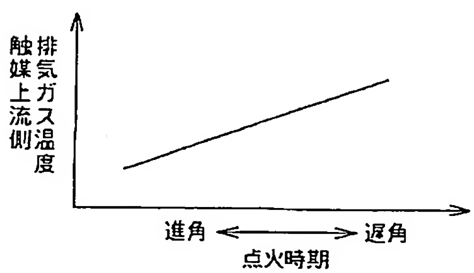

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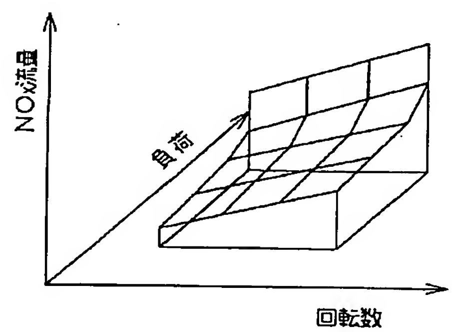

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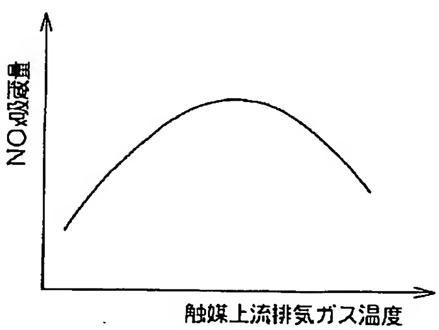

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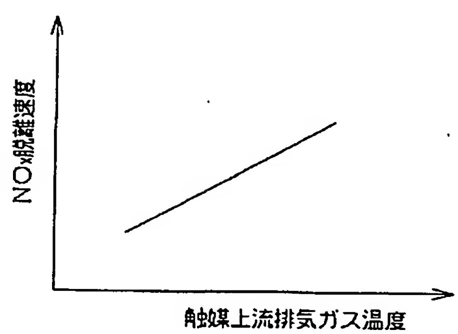

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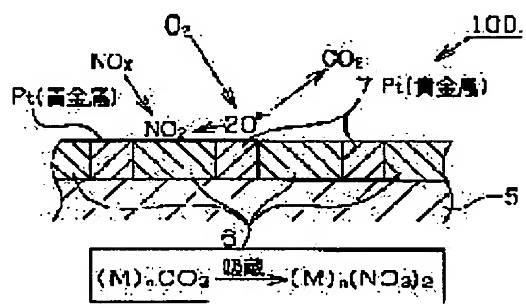
(21)Application number : 11-060260	(71)Applicant : YANMAR DIESEL ENGINE CO LTD
(22)Date of filing : 08.03.1999	(72)Inventor : NISHIMOTO KYOTARO

(54) EXHAUST EMISSION CONTROL METHOD IN INTERNAL COMBUSTION ENGINE

(57)Abstract:
PROBLEM TO BE SOLVED: To promote exhaust purification by comprehending the amount of nitrogen oxides occluded based on the change in oxygen concentration of the exhaust gas detected by oxygen sensors disposed upstream and downstream of nitrogen oxide occlusion reduction catalyst, so as to appropriately obtain the occlusion amount of nitrogen oxides in the catalyst and by selecting the air excess ratio.
SOLUTION: A nitrogen oxides occlusion reducing catalyst 100 carries a first component 6 of carbonate (M)nCO3 and a second component 7 of a noble metal such as platinum on a heat resistance base material 5. When an excess air ratio is in a lean state, oxygen ion and NOX react with each to form NO2. Then the NO2 reacts with carbonates, which is adsorbed to the catalyst 100 to form nitrates. When the nitrates reaches a saturation point, the NOX is desorbed and decomposed after reacting with unburned HC and CO. The change in the oxygen concentration is detected by oxygen sensors at the upstream and downstream sides. When an estimated ratio of NOX occlusion reaches a prescribed value, the air excess ratio is selected from lean to rich state. It is also estimated whether or not the nitrates have been completely desorbed from the catalyst 100, the air excess ratio is selected from rich to lean state.



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CLAIMS

[Claim(s)]
[Claim 1] According to the nitrogen-oxides occlusion reduction catalyst equipped with the 2nd component which consists of the simple substance, oxide, or multiple oxide of the 1st component and noble metals which consists of a carbonate In conditions with the amount of oxygen more superfluous than stoichiometry, change the nitrogen oxides in exhaust gas to a nitrogen dioxide, and occlusion of said nitrogen dioxide is carried out to said 1st component. A nitrogen dioxide is desorbed from said 1st component to which occlusion of the nitrogen dioxide was carried out in the conditions which run short of the amounts of oxygen from stoichiometry. And the carbon monoxide in exhaust gas, In the nitrogen-oxides occlusion reduction catalyst which returns said nitrogen dioxide desorbed with the hydrocarbon Since it is desorbed from the nitrogen oxides by which occlusion was carried out to said 1st component, when an excess air factor is changed from Lean to Rich The oxygen sensor installed in the upstream and the downstream of a nitrogen-oxides occlusion reduction catalyst, respectively detects change of the oxygen density in exhaust gas. The purification approach of the exhaust gas in the internal combustion engine characterized by changing an excess air factor to Lean since rich if the amount of desorption of nitrogen oxides is presumed by change of said oxygen density and said amount of desorption reaches the value set up beforehand.
[Claim 2] The purification approach of the exhaust gas in the internal combustion engine according to claim 1 which multiplies the difference of the reference temperature set up beforehand and the exhaust gas temperature of the downstream of a nitrogen-oxides occlusion reduction catalyst by the predetermined multiplier, adds to the output voltage value of the downstream oxygen sensor of a nitrogen-oxides occlusion reduction catalyst, amends the output voltage value of said downstream oxygen sensor, and is not concerned with the exhaust gas temperature of said downstream oxygen sensor circumference, but detects an exact oxygen density.
[Claim 3] It is set as the time amount which an excess air factor is set [time amount] as Lean for time amount until the ratio of the actual amount of nitrogen-oxides occlusion to the nitrogen-oxides occlusion capacity of a nitrogen-oxides occlusion reduction catalyst becomes a predetermined value, and works an engine. And the purification approach of the exhaust gas of the internal combustion engine according to claim 1 which sets it as the time amount which an excess air factor is richly set [time amount] up for time amount until the ratio of the actual amount of desorption of nitrogen oxides to the nitrogen-oxides occlusion capacity of a nitrogen-oxides occlusion reduction catalyst becomes a predetermined value, and works an engine.
[Claim 4] The purification approach of the exhaust gas in the internal combustion engine according to claim 1 which sets the excess air factor after said change as the rich excess air factor of the field where the desorption rate from the nitrogen-oxides occlusion reduction catalyst of nitrogen oxides is quick in case an excess air factor is changed from Lean to Rich, since it is desorbed from the nitrogen oxides by which occlusion was carried out to the nitrogen-oxides occlusion reduction catalyst.
[Claim 5] The purification approach of the exhaust gas in the internal combustion engine according to claim 1 which works an engine with the excess air factor of the rich field where torque fluctuation is small in case an excess air factor is changed from Lean to Rich, in order to desorb the nitrogen oxides by which occlusion was carried out to the nitrogen-oxides occlusion reduction catalyst.
[Claim 6] in order to desorb the nitrogen oxides by which occlusion was carried out to the nitrogen-oxides occlusion reduction catalyst, when an excess air factor is changed from Lean to Rich, the temperature of a nitrogen-oxides occlusion reduction catalyst is gone up by carrying out the lag of the ignition timing -- making -- nitrogen oxides -- and -- or the purification approach of the exhaust gas of the internal combustion engine according to claim 1 which promotes the desorption of a sulfur oxide.

[Claim 7] The purification approach of the exhaust gas of the internal combustion engine according to claim 1 which does fixed time amount operation of the excess air factor lambda in the lambda= 1.0 neighborhood exhaust gas temperature serves as an elevated temperature before stopping an engine.

[Translation done.]

* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the purification approach of an internal combustion engine's exhaust gas.
[0002]
[Description of the Prior Art] In order to make the nitrogen oxides contained in an internal combustion engine's exhaust gas purify generally, the nitrogen-oxides occlusion reduction catalyst is used. In order to desorb the nitrogen oxides which set up and carried out occlusion of the excess air factor to Lean in order to carry out occlusion of the nitrogen oxides to a nitrogen-oxides occlusion reduction catalyst, and to make it react with the carbon monoxide in air (exhaust gas), and a hydrocarbon and to purify, an excess air factor is set up richly.
[0003] However, there was a limit in the amount of the nitrogen oxides which can carry out occlusion to a nitrogen-oxides occlusion reduction catalyst, and when this occlusion capacity is not grasped but free fixed time amount passed conventionally, the excess air factor was changed to rich or Lean.
[0004] Therefore, even if it is going to carry out occlusion of the nitrogen oxides exceeding the occlusion capacity of a nitrogen-oxides occlusion reduction catalyst, the nitrogen oxides in exhaust gas will bypass a nitrogen-oxides occlusion reduction catalyst, and will be emitted into atmospheric air. Moreover, if an excess air factor works an engine with a rich setup in spite of having completed the desorption of nitrogen oxides (nitrate) from the nitrogen-oxides occlusion reduction catalyst, decline in thermal efficiency will be caused.
[0005]
[Problem(s) to be Solved by the Invention] In view of the above-mentioned situation, this invention grasps the occlusion capacity of the nitrogen oxides of a nitrogen-oxides occlusion reduction catalyst, and aims at offering the purification approach of the exhaust gas in the internal combustion engine which promotes purification of the nitrogen oxides in exhaust gas by changing an excess air factor from Lean to Lean richly, appropriately, since rich.
[0006]
[Means for Solving the Problem] Invention of claim 1 According to the nitrogen-oxides occlusion reduction catalyst equipped with the 2nd component which consists of the simple substance, oxide, or multiple oxide of the 1st component and noble metals which consists of a carbonate In conditions with the amount of oxygen more superfluous than stoichiometry, change the nitrogen oxides in exhaust gas to a nitrogen dioxide, and occlusion of said nitrogen dioxide is carried out to said 1st component. A nitrogen dioxide is desorbed from said 1st component to which occlusion of the nitrogen dioxide was carried out in the conditions which run short of the amounts of oxygen from stoichiometry. And the carbon monoxide in exhaust gas, In the nitrogen-oxides occlusion reduction catalyst which returns said nitrogen dioxide desorbed with the hydrocarbon Since it is desorbed from the nitrogen oxides by which occlusion was carried out to said 1st component, when an excess air factor is changed from Lean to Rich The oxygen sensor installed in the upstream and the downstream of a nitrogen-oxides occlusion reduction catalyst, respectively detects change of the oxygen density in exhaust gas. When the amount of desorption of nitrogen oxides is presumed by change of said oxygen density and said amount of desorption reaches the value set up beforehand, it is the purification approach of the exhaust gas in the internal combustion engine characterized by changing an excess air factor to Lean since rich.
[0007] Invention of claim 2 is the purification approach of the exhaust gas in the internal combustion engine according to claim 1 which multiplies the difference of the reference temperature set up beforehand and the

exhaust gas temperature of the downstream of a nitrogen-oxides occlusion reduction catalyst by the predetermined multiplier, adds to the output voltage value of the downstream oxygen sensor of a nitrogen-oxides occlusion reduction catalyst, amends the output voltage value of said downstream oxygen sensor, and is not concerned with the exhaust gas temperature of said downstream oxygen sensor circumference, but detects an exact oxygen density.
[0008] Invention of claim 3 is set as the time amount which an excess air factor is set [time amount] as Lean for time amount until the ratio of the actual amount of nitrogen-oxides occlusion to the nitrogen-oxides occlusion capacity of a nitrogen-oxides occlusion reduction catalyst becomes a predetermined value, and works an engine. And it is the purification approach of the exhaust gas of the internal combustion engine according to claim 1 which sets it as the time amount which an excess air factor is richly set [time amount] up for time amount until the ratio of the actual amount of desorption of nitrogen oxides to the nitrogen-oxides occlusion capacity of a nitrogen-oxides occlusion reduction catalyst becomes a predetermined value, and works an engine.
[0009] Since it is desorbed from the nitrogen oxides by which occlusion was carried out to the nitrogen-oxides occlusion reduction catalyst, in case invention of claim 4 changes an excess air factor from Lean to Rich, it is the purification approach of the exhaust gas in the internal combustion engine according to claim 1 which sets the excess air factor after said change as the rich excess air factor of the field where the desorption rate from the nitrogen-oxides occlusion reduction catalyst of nitrogen oxides is quick.
[0010] In case invention of claim 5 changes an excess air factor from Lean to Rich in order to desorb the nitrogen oxides by which occlusion was carried out to the nitrogen-oxides occlusion reduction catalyst, it is the purification approach of the exhaust gas in the internal combustion engine according to claim 1 which works an engine with the excess air factor of the rich field where torque fluctuation is small.
[0011] when invention of claim 6 changes an excess air factor from Lean to Rich in order to desorb the nitrogen oxides by which occlusion was carried out to the nitrogen-oxides occlusion reduction catalyst, it goes up the temperature of a nitrogen-oxides occlusion reduction catalyst by carrying out the lag of the ignition timing -- making -- nitrogen oxides -- and -- or it is the purification approach of the exhaust gas of the internal combustion engine according to claim 1 which promotes the desorption of a sulfur oxide.
[0012] Invention of claim 7 is the purification approach of the exhaust gas of the internal combustion engine according to claim 1 which does fixed time amount operation of the excess air factor lambda in the lambda= 1.0 neighborhood exhaust gas temperature serves as an elevated temperature, before stopping an engine.
[0013]
[Embodiment of the Invention] Drawing 1 is the conceptual diagram of the nitrogen-oxides occlusion reduction catalyst 100 (it is hereafter called a catalyst 100) suitable for inventing claims 1-7. A catalyst 100 forms the porosity support layer which becomes the heat-resistant base material 5 which consists of cordierite etc. from gamma alumina, and noble metals, such as Platinum Pt, are supported by the porosity support layer as the carbonate shown with the chemical formula ((M) nCO3) later mentioned as the 1st component 6, and the 2nd component 7.
[0014] In the chemical formula ((M) nCO3) of the carbonate which is the 1st component 6, into the part shown with Notation M For example, transition metals, such as a manganese, iron, cobalt nickel, copper, silver, zinc, and chromium molybdenum tungsten vanadium niobium tantalum cerium lanthanum titanium zirconium, Alkaline earth metal, such as calcium magnesium strontium barium, Rare earth, such as alkali metal, such as lithium sodium potassium rubidium caesium, and a lanthanum yttrium, other aluminum, a silicon, tin, lead, Lynn, or the sulfur are applied. Moreover, as the 2nd component 7, the component which consists of the simple substance of noble metals, such as palladium, a rhodium, and a ruthenium, an oxide, or a multiple oxide in addition to Platinum Pt is applicable.
[0015] Drawing 1 sets an excess air factor as Lean (thin condition), and shows the process which carries out occlusion of the nitrogen oxides (hereafter referred to as NOX) to a catalyst 100 in the form of a nitrate (NO3 salt). Drawing 2 sets an excess air factor as Rich (rich state), desorbs the nitrate by which occlusion was carried out to the catalyst 100 from a catalyst 100, and shows the process to purify.
[0016] Drawing 4 is the front view showing the condition of having installed the catalyst 100 which includes the 1st component 6 and the 2nd component 7 in the middle of the exhaust pipe 2. As shown in drawing 4 , the exhaust pipe 2 is connected to the engine 1, and the upstream oxygen sensor 3 is installed in the side near an engine 1 on both sides of the catalyst 100 of an exhaust pipe 2, and the downstream oxygen sensor 4 is installed in the side far from an engine 1.
[0017] In the Lean condition (thin condition) that the excess air factor lambda was set as lambdaL (drawing 3), on a catalyst 100, as shown in drawing 1 , oxygen ion O2- or O2-, and NOX react, a nitrogen dioxide

NO2 arises, and NO2 reacts with the carbonate which is the 1st component 6 of a catalyst 100, sticks to the front face of a catalyst 100, and forms a nitrate. The reaction formula at this time is expressed like (1) type.
(M) nCO3+2NO2+1/2O2 ->(M) n(NO3)2+CO2 ... (1)
[0018] If the nitrate on a catalyst 100 will be in a saturation state, as shown in drawing 3 , an excess air factor will be set as lambda=lambda R, and it will be desorbed from a nitrate to the nitrogen oxides NOX. The reaction formula at this time is expressed like (2) types.
(M) nCO3+2NO2+1/2O2 <-(M) n(NO3)2+CO2 ... (2)
In this way, by making the nitrogen oxides NOX from which it was desorbed react with the hydrocarbon HC of non-** contained in exhaust gas, and a carbon monoxide CO, the nitrate on a catalyst 100 is disassembled into nitrogen N2, a carbon dioxide CO 2, and water H2O, and it returns, and removes.
[0019] In a formula (1), as for a formula (2), the direction of a reaction to which it goes becomes reverse. Here, how to compute the time amount tL and tR which an excess air factor is set [time amount] as lambdaL and lambdaR, and works an engine 1 is explained.
[0020] A desorption rate will become slow, if a desorption rate becomes quick and the rate of occlusion is conversely smaller, as the actual amount of occlusion to the NOX occlusion capacity of a catalyst 100 is comparatively (it is hereafter called a NOX occlusion rate.) large in case the desorption of a nitrate is started from a catalyst 100 as shown in drawing 6 .
[0021] As shown in a formula (2), in case a nitrate is desorbed from a catalyst 100, it is desorbed also from oxygen. The amount of desorption of the oxygen is proportional to the amount of desorption of a nitrate. When the desorption rate of the oxygen from a catalyst 100 is large, the rate at which the oxygen density of the downstream of a catalyst 100 decreases becomes slow. The upstream oxygen sensor 3 and the downstream oxygen sensor 4 detect change of this oxygen density.
[0022] Time amount after it records the stage which detected the predetermined output voltage value Vd, respectively and the upstream oxygen sensor 3 detects Vd with the upstream oxygen sensor 3 and the downstream oxygen sensor 4 until the downstream oxygen sensor 4 detects Vd is called a time delay td. This time delay td is in a NOX occlusion rate and proportionality, and a time delay td also becomes long, so that a NOX occlusion rate becomes large.
[0023] By the way, in case occlusion of the NOX is carried out to a catalyst 100, an occlusion rate changes with the amounts of NOX(s) by which occlusion has already been carried out. That is, if there are many amounts of occlusion, an occlusion rate is slow, and an occlusion rate is quick if there are few amounts of occlusion. When occlusion progresses to some extent, an occlusion rate becomes slow and it becomes impossible therefore, to carry out occlusion of it efficiently, even if room to still carry out occlusion remains. Then, when it becomes a predetermined rate with a NOX occlusion rate, an excess air factor is changed from Lean to Rich. The change stage (Lean setup time) of the excess air factor corresponding to the predetermined NOX occlusion rate is computed by the following formula (3). If it controls so that a time delay becomes constant value tdt, a NOX occlusion rate is kept constant and it can decide on the time amount (tL) which sets an excess air factor as Lean (lambdaL).
tL(n+1) =tL(n)+C1xsigma(tdt-td (i))/k1 ... (3)
i is the natural number of -(n-k 1+1) n here.
[0024] In case a time delay is measured, the time delay tL (n+1) of eye a time (n+1) adds and amends the value which took and averaged the difference of the target time delay tdt and the i-th time delay to the n-th time delay tL (n). Here, C1 is a predetermined multiplier which arranges a unit, and is determined are completed as a fixed value by tL by experiment. k1 is the count of a change to average (the time delay was measured), i.e., the count which changed the excess air factor from Lean richly.
[0025] On the other hand, in the desorption process which set the excess air factor as Rich (lambdaR), while the nitrate has ****ed, as shown in a formula (2), it is desorbed also from oxygen O2. A desorption rate will become slow if a desorption rate is quick if the desorption rate of a nitrate is-like proportionally and the amount of the nitrate by which occlusion is carried out to the catalyst 100 has many amounts of occlusion, and there are few amounts of occlusion. Therefore, since change of the amount of desorption of oxygen also follows the amount of desorption of a nitrate, if change of an oxygen density is supervised with the output voltage value of the downstream oxygen sensor 4 and an output voltage value is set to VRRC, the desorption of the nitrate from a catalyst 100 will presume what was completed mostly, and will change an excess air factor from it being rich (lambdaR) to Lean (lambdaL).
[0026] It experiments beforehand and the target output voltage value VRRCT is calculated. This target output voltage value VRRCT serves as an index which shows that the desorption of O2 and NOX was completed. As shown in drawing 8 , maximum of the output voltage of each time of the downstream oxygen

sensor 4 is set to VRRC (i), and the desorption time amount (time amount which sets an excess air factor as lambdaR) tR (n+1) until it changes an excess air factor from it being rich (lambdaR) to Lean (lambdaL) next by the formula (4) is computed.
tR(n+1) =tR(n)+C2xsigma(VRRCT-VRRC (i))/k2 ... (4)
i is the natural number to -(n-k2) n here, and C2 is a multiplier for arranging a unit, and is determined are completed as a fixed value by tR by experiment. k2 is the count of a change which is a count of a change which changes an excess air factor from lambdaR to lambdaL, and was sampled among the changes which carried out in the past.
[0027] Sensibility will change in response to the effect of the temperature of the exhaust gas with which the downstream oxygen sensor 4 has passed the catalyst 100. That is, output voltage will become high if output voltage will become low if exhaust gas is an elevated temperature, and it becomes low temperature conversely. However, by amending an output voltage value as follows, it cannot be based on exhaust gas temperature, but a proper output can be obtained.
[0028] The maximum of the output voltage of the downstream oxygen sensor 4 in predetermined temperature (for example, 560 degrees C) is measured beforehand, and this value is set to Vd0. A formula (5) amends the maximum Vd of the downstream output voltage which the engine 1 was worked and was actually measured. TR is the exhaust gas temperature of the downstream oxygen sensor 4 neighborhood.
Vd=Vd0+C3x (560-TR) ... (5)
C3 is the predetermined multiplier it decided [multiplier] by carrying out output voltage at the time of setting it as the temperature of some [an experiment] and measuring that it would be reference here.
[0029] A formula (6) amends the target output voltage value VRRCT, and it is made to change with exhaust gas temperatures.
VRRCT=VRRCT0+C4x (560-TR) ... (6)
VRRCT0 is a target output voltage value at the time of exhaust gas temperature being 560 degrees C here.
[0030] An engine 1 has low exhaust gas temperature during operation at low load low rotation, and it becomes easy to change the output voltage value of the downstream oxygen sensor 4. In this case, a formula (7) and (8) amend the counts k1 and k2 of a change of an excess air factor to k10 and k20, respectively.
k10=k1xC5 (560-TR) ... (7)
k20=k2xC6 (560-TR) ... (8)
C5 and C6 are predetermined multipliers here.
[0031] since it is desorbed from the nitrate which carried out occlusion to the catalyst 100 -- an excess air factor -- from Lean (lambdaL) -- being rich (lambdaR) -- if a desorption rate is quick in case it changes -- the part -- it is rich, the time amount which must be worked becomes short, and the time amount which can be worked by Lean becomes long. As shown in drawing 9 , the desorption rate of NOX from a catalyst 100 becomes so large that an excess air factor becomes rich. Therefore, in case an excess air factor is set as Rich (lambdaR), it is set as lambdaR=0.8. Although what is necessary is just to set up lambdaR by within the limits to 0.65-0.9, it is more desirable to set up within the limits of 0.7-0.85.
[0032] Moreover, as shown in drawing 10 , as for torque fluctuation, an excess air factor serves as max in the lambda= 1 neighborhood. Therefore, in case a nitrate is desorbed from a catalyst 100, near [large / lambda= 1] torque fluctuation is avoided, and lambdaR is set as 0.8. Although what is necessary is just to set up lambdaR by within the limits to 0.65-0.9 in order to make torque fluctuation small, it is more desirable to set up within the limits of 0.7-0.85.
[0033] The temperature of the exhaust gas of the upstream of a catalyst 100 becomes high, so that the lag of the ignition timing is carried out, as shown in drawing 11 . Since the desorption rate of the nitrate from a catalyst 100 becomes quick so that exhaust gas temperature is high, when an excess air factor is set as Rich (lambdaR), the lag of the ignition timing is carried out.
[0034] As shown in drawing 12 , the NOX flow rate of the upstream of a catalyst 100 becomes so large that a load and an engine rotational frequency are large. Moreover, the exhaust gas temperature of the upstream of a catalyst 100 becomes high, so that a load and an engine rotational frequency are large. As shown in drawing 13 , the amount of NOX occlusion of a catalyst 100 changes with the temperature of this exhaust gas.
[0035] Time amount (time amount taken to carry out occlusion of the NOX to some extent) until it becomes a value with (the amount of NOX occlusion / NOX occlusion capacity) is proportional to not being based on a load and an engine rotational frequency (NOX occlusion capacity / NOX flow rate). Therefore, if the value which carried out the multiplication of the time amount tL (drawing 3 R> 3) which sets an excess air factor as Lean (lambdaL) to the RIN counter multiplier CLt proportional to (a NOX flow rate / NOX occlusion

capacity) is integrated, the addition value is proportional to not being based on a load and an engine rotational frequency (the amount of NOX occlusion / NOX occlusion capacity).
[0036] therefore, the time of calculating beforehand the addition value corresponding to the value (CLtxtL) of predetermined (amount of NOX occlusion / NOX occlusion capacity) in the experiment, and the addition value of (CLtxtL) turning into the value -- an excess air factor -- from Lean (lambdaL) -- being rich (lambdaR) -- if it changes, a catalyst 100 can start desorption in the condition near the occlusion limitation or occlusion limitation of NOX, and the NOX purification in exhaust gas will become very efficient. tL is time amount which sets the excess air factor as Lean (lambdaL) here.
[0037] Moreover, when an excess air factor is set as Rich (lambdaR), the NOX desorption rate from a catalyst 100 will become quick as shown in drawing 14 , if exhaust gas temperature becomes high. therefore, the rich counter multiplier CRt proportional to (a NOX desorption rate / NOX occlusion capacity) -- an excess air factor -- being rich (lambdaR) -- the value which carried out the multiplication of the time amount tR (drawing 3) to set up, and integrated it is proportional to not being based on a load and an engine rotational frequency (the amount of NOX desorption / NOX occlusion capacity).
[0038] Therefore, the addition value corresponding to the value (CRtxtR) of predetermined (amount of NOX desorption / NOX occlusion capacity) is beforehand calculated in the experiment, and when the addition value of (CRtxtR) turns into the value, an excess air factor is changed from it being rich (lambdaR) to Lean (lambdaL). Thereby, the desorption of NOX can be mostly completed from a catalyst 100, and it can move to an occlusion process.
[0039] As shown in drawing 5 , in the Lean condition, not only NOX but sulfur S, oxygen ion O2-, or O2- reacts, and an excess air factor forms a sulfate on a catalyst 100, and adsorbs (poisoning). If a sulfate is formed on a catalyst 100, since the fields where only the part can carry out occlusion of the nitrate will decrease in number, the occlusion capacity of NOX </SUB> will become small.
[0040] The desorption rate of the sulfate from a catalyst 100 becomes so quick that the exhaust gas temperature of the catalyst upstream is high. Therefore, if the lag of the ignition timing is carried out in order to make exhaust gas temperature high, the desorption rate of a sulfate will become quick and the NOX occlusion capacity of a catalyst 100 will return to the original capacity.
[0041] Even if it works an engine 1 again and the temperature of a catalyst 100 rises, it becomes impossible to desorb these, in order that a catalyst 100, a nitrate, and a sulfate may join together strongly, if a catalyst 100 is made to suspend the engine 1 (drawing 4) under operation in the condition that the nitrate and the sulfate are formed. Therefore, since a certain fixed time amount (preferably for example, for 1 - 5 minutes for 2 - 3 minutes) excess air factor lambda is desorbed from 1.1 to 0.9, NOX which sets it as the range of 1.0-0.95 preferably, was worked, and carried out occlusion, or the sulfur oxide which carried out poisoning, it is made to make it stop, in case the engine 1 under operation is stopped.
[0042] Although noble metals, such as Pt which is the 2nd component 7, explained based on the configuration currently supported by the direct thermal-resistance base material 5, the 1st component 6 may be made to support the 2nd component 7 with the above explanation, as shown in drawing 7 .
[0043]
[Effect of the Invention] If invention of claim 1 is applied, since an oxygen sensor will detect the amount of desorption of the oxygen proportional to the amount of desorption of the nitrogen oxides in exhaust gas After being able to presume the amount of occlusion of the nitrogen oxides to a catalyst 100, setting an excess air factor as Lean to the occlusion limitation of a catalyst 100 and working an engine, it changes richly. Since rich and an excess air factor can be changed to Lean when the desorption of the nitrogen oxides from a catalyst 100 is completed, the nitrogen-oxides purification engine performance of a catalyst 100 can fully be demonstrated, and exhaust gas can be purified efficiently. Moreover, since time amount which an excess air factor is changed [time amount] richly and works an engine can be made into necessary minimum, thermal efficiency can be raised.
[0044] If invention of claim 2 is applied, even if it changes exhaust gas temperature, it can amend to the detection value at the time of measuring the detection result of the downstream oxygen sensor 4 with reference temperature, therefore the amount of the nitrogen oxides in exhaust gas can be presumed correctly.

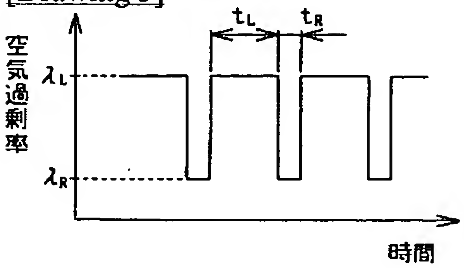
[0045] Since an excess air factor can be richly changed from Lean appropriately so that the nitrogen oxides which secured and carried out occlusion of the amount of occlusion corresponding to the nitrogen-oxides occlusion capacity of a catalyst 100 may be desorbed even if the load concerning an engine and an engine rotational frequency change and the flow rate of nitrogen oxides changes if invention of claim 3 is applied, the nitrogen oxides in exhaust gas can be purified efficiently.

[0046] If invention of claim 4 is applied, thermal efficiency can be raised by being able to perform desorption of the nitrogen oxides from a catalyst 100 quickly, and shortening time amount which can be made to increase the amount of occlusion of the nitrogen oxides per unit time amount, and can promote purification of exhaust gas, and sets up the excess air factor richly, since time amount which sets up the excess air factor richly can be shortened.
[0047] If invention of claim 5 is applied, since torque fluctuation will work an engine 1 with a small rich excess air factor, torque fluctuation can be suppressed in case desorption of nitrogen oxides is performed.
[0048] If invention of claim 6 is applied, since it will carry out the lag of the ignition timing and the temperature (temperature of exhaust gas) of a catalyst 100 will be raised Since the desorption of nitrogen oxides can be promoted from a catalyst 100, time amount which sets up the excess air factor richly can be shortened and time amount which an excess air factor is set [time amount] as Lean and works an engine 1 can be lengthened Purification of the nitrogen oxides in exhaust gas can be promoted, and thermal efficiency can be raised.
[0049] Since an engine will be suspended after desorbing the nitrogen oxides by which occlusion is carried out to the catalyst 100, and the sulfur oxide which carried out poisoning if invention of claim 7 is applied, a catalyst 100 is maintained at a clean condition, the occlusion capacity to nitrogen oxides can fully be secured, and when working an engine 1 next time, the nitrogen oxides in exhaust gas can be purified efficiently.

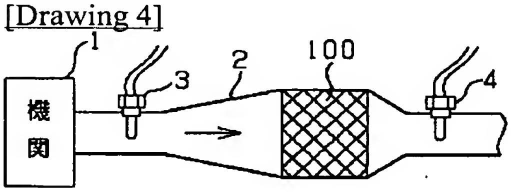
[Translation done.]

DRAWINGS

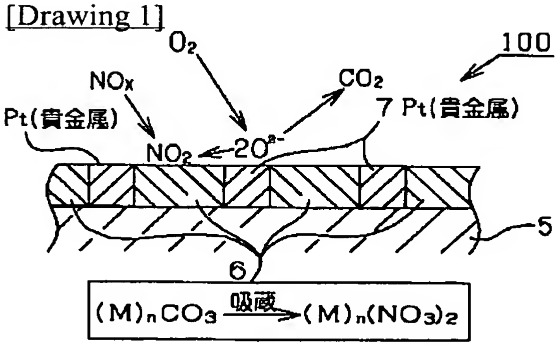
[Drawing 3]



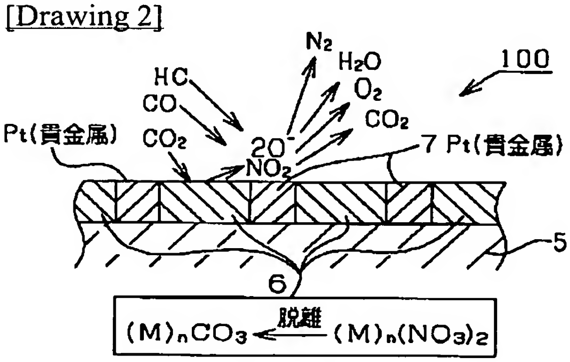
[Drawing 4]



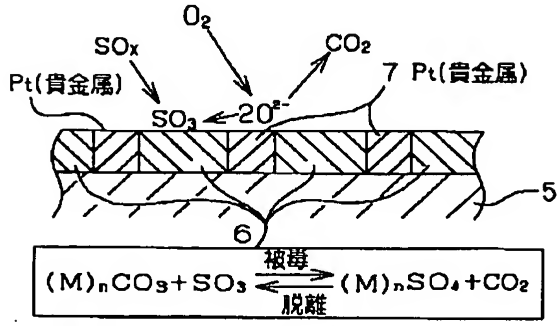
[Drawing 1]



[Drawing 2]



[Drawing 5]



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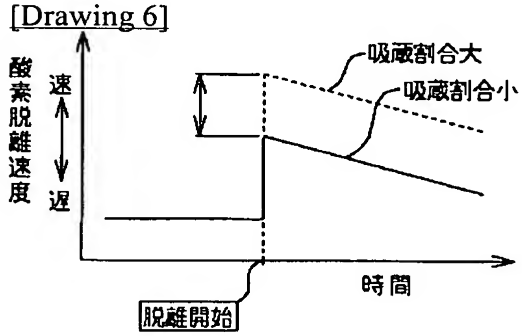
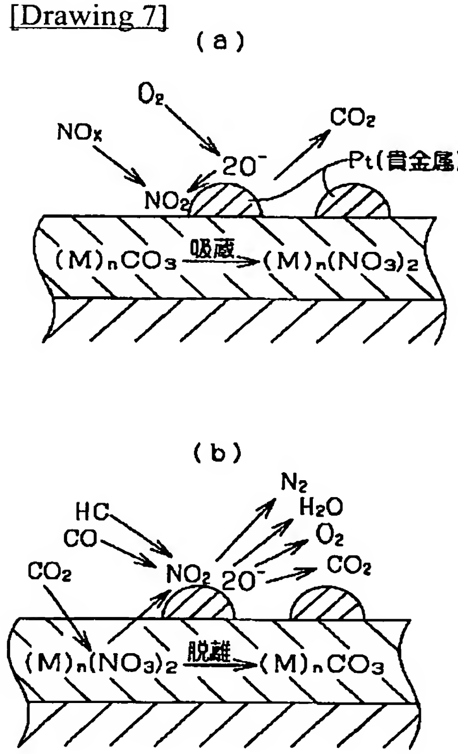
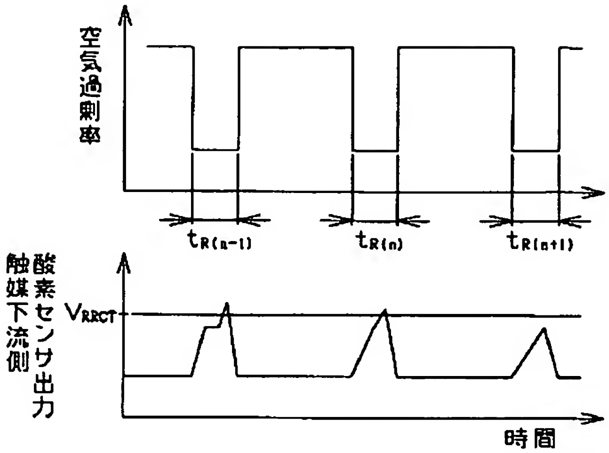


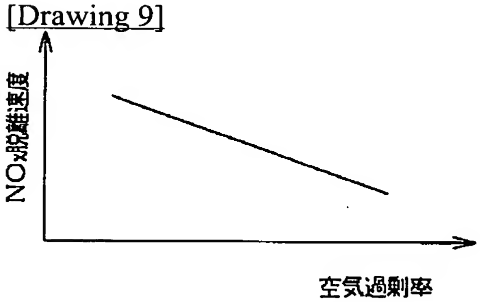
[Drawing 7]



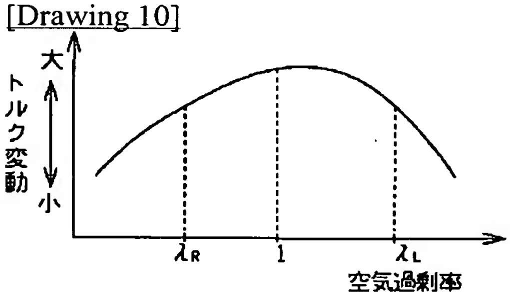
[Drawing 8]



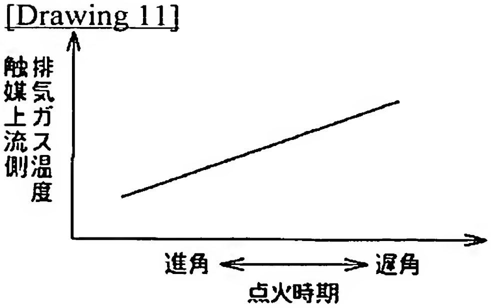
[Drawing 9]



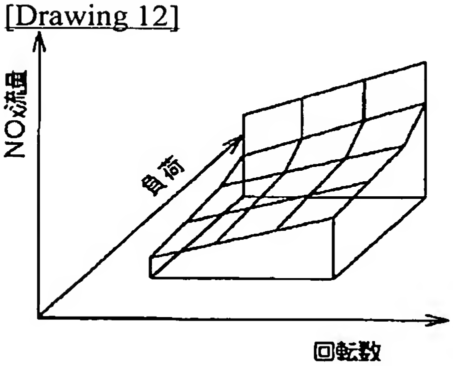
[Drawing 10]



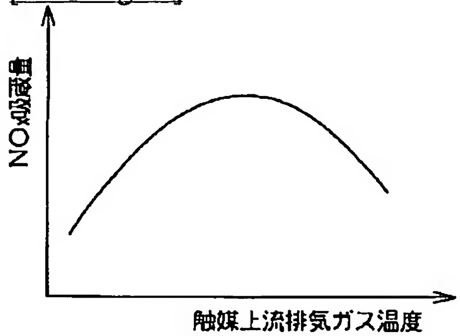
[Drawing 11]



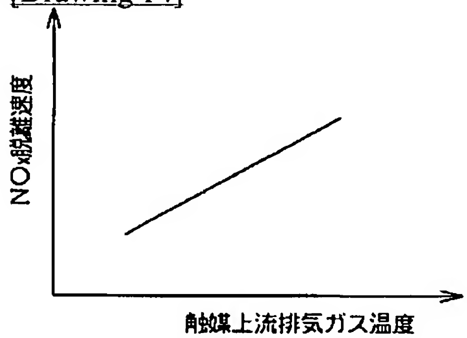
[Drawing 12]



[Drawing 13]



[Drawing 14]



[Translation done.]